Selective Color Removal Nanofiltration Membrane for the 7 MGD Irvine Ranch Water Treatment Project

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ABSTRACT

A new polyether sulfone membrane which was recently developed, has now been used for the purification of colored groundwater. This new nanofiltration membrane was developed to selectively remove organic material with molecular weight greater than 1000 daltons, while passing most salts. This characteristic is ideal for applications which have low salinity, but high color or other organic compounds. This membrane differs from traditional polyamide RO membranes as it is chlorine tolerant and has a large negative surface charge. This makes it ideal for waters containing high organic levels.

This membrane has been extensively pilot tested with other traditional nanofiltration membranes. The membrane had the best combination of high flux, high color removal and minimal hardness removal. As a result of these features the membrane was selected for a 27.8 ML (7.35 mgd) water treatment plant at the Irvine Ranch Water District. The full-scale plant contains about 1300 pieces of 33.9 square meters (365 sq feet) spiral wound elements. The full-scale plant has been completed and start-up of the first train has been completed. The feed color units (CU) were in excess of 200 CU, while the permeate was less than 5 CU, which meets the requirement of the plant. This is one of the largest membrane plants designed to only remove color from the water.

KEY WORDS

Nanofiltration, Color Removal, Chlorine Tolerant Membrane

INTRODUCTION

Membrane technology has become a mature technology for the treatment of a variety of brackish water sources, due in large part to the favorable economics of low pressure membranes and the ability of these membranes to selectively remove dissolved species. However, the demands on membrane performance continue to increase as water quality requirements tighten and system designs become more complex. Traditionally, this has meant that the reverse osmosis (RO) membranes need to have higher rejection for better dissolved salt removal. In addition to this performance trend, new applications have developed which require selective removal of certain dissolved species, such as hardness, iron, natural organic matter (NOM), pesticides, trihalomethane formation potential (THMFP) and organic material which causes color. In these cases, engineers desire high removal of specific contaminants, but want to maintain some level of salts in the water so that the water does not become aggressive, which can cause corrosion problems with piping in the distribution network.

A variety of nanofiltration (NF) membranes are available which successfully soften waters high in calcium and magnesium scale. Many such plants are operating throughout the world, especially in Florida. Such membranes are often characterized by low monovalent salt rejections (80-90%), but high divalent ion rejections (>95%). Traditionally, these membranes are used in applications where the feedwater has hardness in the range of 200 – 400 mg/L as calcium carbonate, and requires a permeate with 70 – 100 mg/L as calcium carbonate. These nanofiltration membranes also have good selectivity for NOM and THMFP organic compounds, as well as iron. Thus, they are an ideal treatment technology. There are, however, other surface water sources which have fairly low levels of hardness and salinity, but have high levels of organic material which cause color. Organic material can be found in groundwater sources which have surface water intrusion, or groundwater sources which are influenced by decomposing vegetative materials. The contamination of these waters is measured in terms of color units. Natural waters which are high in color may typically have 100 to 400 CU, while an acceptable water would be characterized as having less than 5 CU. At this level, the color in the water is imperceptible to the human eye.

New nanofiltration membranes are desired for the treatment of colored waters which are low in salinity because current RO and NF membranes will remove too much salinity and result in an aggressive water that would have to be recarbonated. Such a membrane was required for the 27.8 ML treatment project at Irvine Ranch Water District. This community located in southern California planned to augment their water supply with water from a deep aquifer. This well water had an acceptable salinity which ranged from 250 to 500 mg/L of total dissolved solids (TDS) and a calcium level of 13 mg/L, but had high color, ranging from 250-400 color units. This application was ideal for a class of membrane which is based on highly charged, sulfonated polyethersulfone (SPES) membrane. Such membranes have been previously developed, (Ikeda, et al 1988) and have shown low salt rejections for mixed ions solutions. This membrane has relatively low rejection of ionic species, especially in the presence of divalent cations, but high rejection of low molecular weight organic compounds. The former characteristic is advantageous compared to RO or NF membranes, while the latter is far superior to UF membranes.

MEMBRANE CHARACTERIZATION

The new membrane considered for the Irvine Ranch water treatment project was the HydraCoRe membrane made by Hydranautics. This is a specially formulated sulfonated polyethersulfone, thin film composite membrane. The properties of the membrane are unique and well-suited to this application. The absence of a typical polyamide barrier layer results in improved fouling resistance, chemical cleanability and disinfection compatibility.

Surface Characterization

The charge on the surface of the membrane is strongly negative due to the presence of the sulfonate functional groups. Streaming potential measurements for this membrane are given in Figure 1, as well as comparative values for standard and low fouling polyamide thin film composite membranes. This data shows that the SPES membrane has a surface zeta potential charge of –85 mV over a pH range of 3 to 11. In comparison, a conventional polyamide RO membrane had a zeta potential of +10 mV at pH 3 and –20 mV for pH 6 or greater. The large negative charge of the SPES membrane is desired since the NOM in most source waters is composed of humic acids. It is expected that the strong negative charge of the membrane surface will repel the negatively charged humic acid compounds, and thus minimize fouling by organic adsorption.

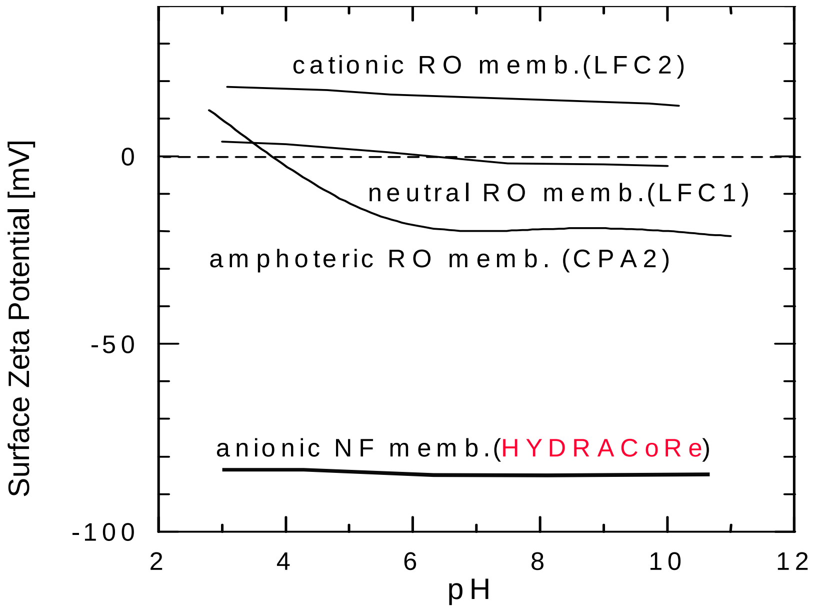

Figure 1 Surface Zeta potential measurement for RO and new NF membranes

Ion Separation Properties

The SPES membrane is a fairly loose NF membrane, and derives a significant degree of dissolved salt rejection from the charge repulsion mechanism. The presence of various ion species does have a dramatic affect on the actual selectivity of the membrane. This is shown in Table 1. The rejection of each ionic solution was determined in cell tests with flat sheet pieces of membrane. The ionic mixture was prepared at a feed concentration of 2000 mg/L at a pH of 6.5. The applied pressure was 1 MPa (144 psi) and a temperature of 25 C.

The effect of the ion size and charge on the membrane selectivity is clearly seen in Table 1. The rejection for sodium chloride is 50% while the rejection of sodium sulfate is 90%. This can be explained by the strong negative charge of the membrane surface having greater repulsion of the large, divalent sulfate ion, compared to the smaller monovalent chloride ion. In contrast, the rejection of a calcium chloride solution was only 12% compared to 50% rejection for sodium chloride. In this case the larger divalent calcium ion results in a lower membrane rejection compared to the smaller, monovalent sodium.

The factor important for causing this effect is the stronger attraction between the membrane surface and the positively charged calcium ion. In particular, the charge at the membrane surface is thought to be somewhat neutralized by the calcium ions, thus minimizing the rejection due to charge. Based on this understanding, another expected effect is the reduction in salt rejection as the feed concentration increases. Various experiments have been done on model and actual surface water mixtures. For example, the membrane had 40% rejection for a 500 ppm TDS surface water, while the rejection dropped to 20% for a 2000 ppm TDS surface water. In a full-scale system, recovery is generally greater than 80%, which means that the concentrate is 4 to 6 times more

Table 1 Rejection characterization of various ionic pair solutions by HydraCoRe

Anion / Cation			A^-	A^{2-}
			Cl	SO_4
		Molecular Weight	35	96
M^+	Na	23	50%	90%
M^{2+}	Mg	24	20%	35%
	Ca	40	12%	-

concentrated than the feed, and thus the permeate TDS will approach the TDS of the initial RO feed. Thus, a full-scale NF system utilizing the HydraCoRe membrane will not significantly alter the ion composition of the feedwater. For specific projects with low feed salinity, this is preferred as explained earlier.

Chemical Stability

The advantage of a SPES membrane is the greater stability toward pH and chlorine, compared to conventional polyamide membrane. Chlorine is especially harmful to polyamide membranes due to the hydrolysis of the polyamide and resulting increase in salt passage. Polyamide RO membranes will typically be limited to an exposure less than 0.01 ppm chlorine. A general rule is that the salt passage of polyamide membranes doubles for an exposure of 2000 ppm-hours of free chlorine. As a result, low doses of chlorine cannot be used to to control biofouling for polyamide membranes, and chlorine cannot be used to clean organic or biologically fouled polyamide membranes. In contrast the SPES membrane is a very chlorine tolerant membrane. A test was done by soaking the SPES membrane in a 1000 ppm sodium hypochlorite solution. The membrane retained the same rejection over 50 days of exposure. For comparison, a cellulose acetate membrane was exposed to a 100 ppm sodium hypochlorite solution, and had a doubling of salt passage in 10 days (24,000 ppm hour tolerance). Thus, the SPES membrane is ideally suited to low doses of chlorine to control biofouling or higher doses of chlorine to improve organic foulant removal. This will greatly enhance the application of this membrane for difficult waters.

LABORATORY AND PILOT TESTING WITH IRVINE RANCH WATER

An extensive pilot test was carried out to evaluate various nanofiltration membranes for the treatment of the deep well water at the Irvine Ranch site. (Fu 1995) The water contained about 250 ppm of TDS, calcium of 13 mg/L, but had high total organic carbon (TOC of 10 mg/L) and high color (200 CU). The goal of this study was to reduce the color units to less than five, while not significantly affecting the salinity of the water. Results of the pilot test indicated that the HydraCoRe elements could reduce this water to less than 5 CU even at greater than 80% recovery. In addition, the HydraCoRe membrane did not significantly change the salinity of the water. The feed conductivity was reduced from 500 to 350 and calcium was reduced from 13 to 8.5 mg/L. In comparison a conventional polyamide NF membrane was also able to reduce the CU to less than 5, but the permeate conductivity was 48 uS/cm and the calcium was 0.2 mg/L. The low salinity and hardness of such a water will make it aggressive and would require that the customer utilize recabonation to stabilize the water, hence adding additional cost, chemical handling and new sources of contamination. The specific flux of the membrane was 10.6 lmh/bar (0.43 gfd/psi), which is comparable to other nanofiltration membranes. The two-stage RO pilot unit was operated continuously for more than 5 months and demonstrated stable performance, as well as showing that the fouled membrane could be cleaned to its original performance levels. In addition, samples of water from the well site were collected and used for flat sheet membrane testing in our laboratory. The water samples were concentrated with a HydraCoRe element to achieve 3 different levels of higher color and TDS. These three solutions were then used in the flat sheet tests. The results of the test are shown in Figure 2. The cell tests were carried out at 0.52MPa feed pressure and 25 C.

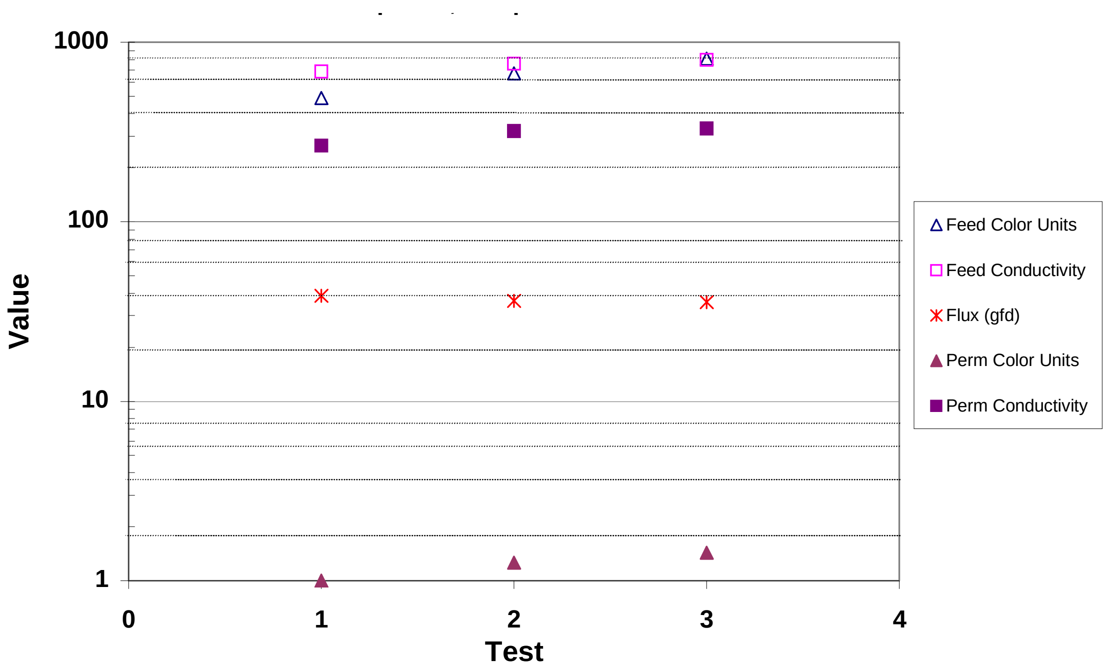

Figure 2 Lab Test with Flat Sheet HydraCoRe Membrane and Irvine Ranch Water.

The data show that the color of the feed water was initially 450 CU, and was reduced to <1 CU. At 850 CU in the feed, the permeate was 1.5 ppm CU, yielding 99.8% rejection of organic color compounds. The conductivity rejection decreases as the feed concentration increases. At a conductivity of 700 µS/cm, the rejection is 61%, while at 800 µS/cm the conductivity rejection is about 55%. The flux for all tests was approximately 67.8 lmh (40 gfd). This data confirmed that the membrane was suitable for the Irvine Ranch water treatment project.

IRVINE RANCH FULL-SCALE PLANT

Based on the successful pilot testing, the Irvine Ranch Water District selected the new SPES membrane for their full-scale plant. The system design information is given in Table 2. The plant was constructed and will start-up during January – February 2002. Operational data from the first six months has been favorable. The start-up pressure was 96 psi, and the plant produced about 386 m3/hr (1700 gpm) of permeate. The color in the feed (greater than 280) was reduced to about 3 CU in the permeate, as desired. During the first 6 months of operation, the membranes have consistently made the water quality targets and the membranes have not needed to be cleaned. Data from this operation period (Table 3) shows very stable performance.

Table 2 Irvine Ranch RO System design parameters

Parameter	Design
Array	36 x 18 x 7
Flux	26.3 lmh
Feed TDS	365 mg/L
Permeate TDS	352 mg/L
Feed Pressure	0.52 MPa
Total Elements	1300 pcs, 33.9 sq m each

POTENTIAL APPLICATIONS FOR THE SPES MEMBRANE

The unique characteristics of the SPES membrane, as discussed earlier, make it suitable for a wide range of applications. Some of these are now being explored; one such example is the use of this membrane to remove pesticides from low TDS groundwaters. Preliminary data has been presented which shows that rejection varies significantly depending on the size and chemical nature of the pesticide. (Kiso 2001) Other applications which are being investigated include dye separations, purification of highly colored streams from pulp and paper manufacturing, sugar fractionation, and color removal from soy sauce. These applications share the common need of removing organic molecules which have molecular weights larger than 1000 daltons. SPES membranes are especially suited for these applications because of the strong negative surface charge and the robust chemical resistance, even to hypochlorite.

CONCLUSION

The development of the new SPES membrane has given engineers a unique new membrane which has relatively low salt rejections, but high rejection of naturally occurring organic material. This is an ideal product for color removal in potable water sources which are low in TDS. The membrane was successfully pilot tested and then scale-up to a 27.8 ML commercial plant.

ACKNOWLEDGEMENTS

The authors wish to thank Carl Spangenberger of the Irvine Ranch Water District for providing operating data from the membrane plant.

Table 3A Metric Measure

Irvine Ranch Water District Deep Aquifer Treatment System: Plant Data from Start-up				
Date:		**8-Feb**	**5-May**	**14-Aug**
Pressure (bar)	Feed Stage 1	7.04	6.65	6.19
	Feed Stage 2	5.16	4.88	4.55
	Feed Stage 3	3.91	3.66	3.42
	Permeate Stage 1	1.05	1.01	0.93
	Permeate Stage 2	1.12	1.06	1.01
	Permeate Combined	0.68	0.62	0.59
	Concentrate Stage 3	2.70	0.43	2.31
Δ P (bar)	Cartridge Filters	0.09	0.07	0.07
	Stage 1	1.88	1.78	1.64
	Stage 2	1.25	1.22	1.13
	Stage 3	1.22	1.15	1.11
Flow (m3/hr)	Permeate Stage 1	263.9	254.3	252.9
	Permeate Stage 2	102.1	91.3	88.5
	Permeate Combined	386.3	386.9	382.0
	Concentrate	34.5	33.4	33.2
	Feed (Perm + Conc)	420.9	420.3	415.2
	Recovery	91.79	92.06	92.01
Conductivity (mS/m)	Feed	570	592	637
	Permeate	527	535	536.7
	Concentrate	1468.6	1331	1342
Color (cu)	Feed	342	235	238
	Feed Brine Avg	1588.5	1467.5	1529
	Permeate	3	2	2
	Concentrate	2835	2700	2820
pH	Feed	8.8	6.98	8.08
	Permeate	8.47	6.78	8.6
	Concentrate	8.6	6.45	8.59
Feed Water	Cl_2 (mg/L)	0	0	0
	SDI (5)-(10)-(15)	3.70	3.95	NA
	Turbidity (NTU)	0.742	0.65	0.77
	Temperature (°C)	32.8	31.9	31.9

Table 3B US/English Measure

Irvine Ranch Water District Deep Aquifer Treatment System: Plant Data from Start-up				
Date:		**8-Feb**	**5-May**	**14-Aug**
Pressure (psig)	Feed Stage 1	102.1	96.4	89.8
	Feed Stage 2	74.85	70.7	66
	Feed Stage 3	56.73	53	49.6
	Permeate Stage 1	15.26	14.7	13.5
	Permeate Stage 2	16.18	15.3	14.6
	Permeate Combined	9.79	9	8.6
	Concentrate Stage 3	39.1	6.3	33.5
Δ P (psig)	Cartridge Filters	1.32	1.07	1.02
	Stage 1	27.25	25.74	23.76
	Stage 2	18.12	17.7	16.43
	Stage 3	17.63	16.68	16.09
Flow (gpm)	Permeate Stage 1	1163.7	1121.25	1115.02
	Permeate Stage 2	450.1	402.64	390.18
	Permeate Combined	1703.3	1705.98	1684.49
	Concentrate	152.3	147.11	146.23
	Feed (Perm + Conc)	1855.6	1853.09	1830.72
	Recovery	91.79	92.06	92.01
Conductivity (mS/m)	Feed	570	592	637
	Permeate	527	535	536.7
	Concentrate	1468.6	1331	1342
Color (cu)	Feed	342	235	238
	Feed Brine Avg	1588.5	1467.5	1529
	Permeate	3	2	2
	Concentrate	2835	2700	2820
pH	Feed	8.8	6.98	8.08
	Permeate	8.47	6.78	8.6
	Concentrate	8.6	6.45	8.59
Feed Water	Cl_2 (mg/L)	0	0	0
	SDI (5)-(10)-(15)	3.70	3.95	NA
	Turbidity (NTU)	0.742	0.65	0.77
	Temperature (°F)	91.03	89.38	89.35

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REFERENCES

Fu, P., Ruiz, H., Lozier, J., Thompson, K., and Spangenberg, C*.,* (1995) *"A pilot study on ground water natural organics removal by low-pressure membranes. Desalination* (1995) 47-56.

Ikeda, K., Nakano, T., Ito, H, Kubota, T., and Yamamoto, S., (1988) *New composite charged reverse osmosis membrane. Desalination 68* (1988) 109-119.

Kiso, Y., Sugiura, Y., Kiato, T., and Nishimira, K., (2001) *Effect of hydrophobicity and molecular size on rejection of aromatic pesticides with nanofiltration membranes. Journal of Membrane Science 192* (2001) 1-10.